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Plasmon induced enhancement of the electroluminescence signal of thin insulating polypropylene films*

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Abstract— Chemical defects are of deleterious nature for the electrical properties of insulating polymers and can largely degrade their performance. Although these defects usually leave spectroscopic signatures in terms of characteristic luminescence peaks, it is nontrivial to assign, in an unambiguous way, the peaks to specific groups of defects because of the low intensity of the signal. In this work, we go beyond the traditional electroluminescence technique to record spectroscopic features of insulating polymers. By introducing a single plan of silver nanoparticles (AgNPs) at the near-surface of thin polypropylene films, the electroluminescent signal is enhanced by plasmon-related process. The latter leads much higher intensity and phase-stabilization of the recorded spectra, thus improving the assignment of characteristic luminescence peaks.

I. INTRODUCTION

Insulating polymers are widely used in electrical engineering applications, such as high voltage direct current (HVDC) electrical cables, generators, transformers, capacitors, etc. [1]. However, their service life in systems is limited by the stresses (electrical, thermal, mechanical, etc.) they undergo. Knowledge on the response of insulation materials, and in particular insulating polymers to the applied electrical stresses is essential to determine their safety limits. These materials should sustain very high electric fields. For example, the typical service fields for HVDC cables are in the order of 20 kV/mm. With time the ability of insulating polymers to sustain high electric fields decreases. It is mainly due to gradual degradation of the insulating materials and often leads to electrical breakdown. However, the degradation process takes certain time and is accompanied by modification in the response of the materials to the electrical stress. Moreover, the pre-breakdown patterns may differ depending on the situation and the environmental factors (humidity, oxygen, radiation, corrosive agents, etc.) Electrical aging and degradation of insulating polymers therefore represent a constant interest in order to understand the fundamental mechanisms behind these effects, originating from evolving in time defects of the materials, and to contribute to the design and engineering of highly-performant electrical systems.

Electrical aging in insulators results from the induced thermal and higher energy chemical reactions after interaction of charged carriers with the dielectric material [2 – 4]. The aging of insulating polymers under electrical

stress can partially be assigned to the space charges effect in the material. Different diagnostic methods are currently available to probe space charge, like wave propagation techniques (either pressure-wave –PIPWP– or pulsed electroacoustic –PEA– methods) or thermal methods (Laser Induced Modulation Method –LIMM– or Thermal Pulse –TP–) [5]. In the last few years, electrical modes derived from Atomic Force Microscopy (AFM), like Kelvin Force Microscopy (KPFM) [6, 7] and Electrostatic Force Distance Curve (EFDC) [8] advanced on the subject by revealing information on the charge injection and transport processes at nanoscale level. However, given the principle of operation, the above mentioned methods can reveal the presence of space charge but they are not sensitive to the energetics of charge carriers.

As demonstrated previously, the electroluminescence (EL) appears appropriate diagnostic tool to address the aging problem of insulating polymers because the degradation process involves energy dissipation in the chemical bond energy range (of a few eV) that corresponds to the UV-vis range of the optical spectrum [9 – 15]. EL is the excitation of luminescence as a result of the existence of an applied potential difference in the probed material. Basically the EL emission is a dynamic response of charges transport in the polymer material. The appearance of EL can be considered as a sign for the beginning of aging of polyolefin polymers under electrical stress. Spectroscopic analyses thus give indication on the nature of the transition process, *i.e.*, on the dissociative versus non-dissociative excited states relaxation, defining in that way the energy decay mechanism: chemical versus physical one.

The EL of insulating polymers, such as polyethylene and polypropylene, is a specific response of the material which shows charge-structure interactions including the relaxation of kinetic energy by hot carriers, or modifications in their potential energy during radiative recombination of charges [11 – 15]. However, one of the challenges to meet when applying EL to probe aging mechanisms of polyolefin polymers is the low intensity of the obtained signal [14, 15]. This problem is even more complex in the case of polyethylene and polypropylene, as these are weakly emitting materials under electrical field. As a result, the resolution of recorded spectra does not allow fine interpretation. To overcome this problem, we present in this paper a study on the possibility to analyze the

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spectroscopic signature of insulating polypropylene films by plasmon induced enhancement of their characteristic EL spectra.

II. EXPERIMENTAL PART

A. Description of the structure and the plasma process

The insulating polymer material under study was a thin bi-oriented polypropylene (BOPP) film (thickness of 17.8 μm). The BOPP film, provided by KOPAFILM, Germany, was with different roughness for the two faces.

A very thin nanocomposite layer, consisting of a single layer of silver nanoparticles (AgNPs) embedded in a very thin organosilicon (SiOC:H) matrix, was deposited on the side of larger roughness of the BOPP film by a plasma process. To perform the EL-measurements the structure was both sides covered by 100 nm-thick ITO layers with 90% transparency and resistivity of $16 \times 10^{-3} \Omega/\text{cm}^2$. A schematic cross-view of the structure is shown in Figure 1(a) and an optical image on top of the final sample is given on Figure 1(b).

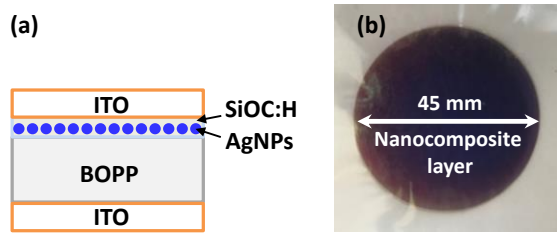


Figure 1. (a) Schematic of the studied structure in cross-section view and (b) Optical image of the final sample taken on the top.

The nanocomposite layer was deposited in two steps process: 1-plasma sputtering to create the layer of AgNPs and 2-plasma polymerization of hexamethyldisiloxane (HMDSO) precursor to cover the AgNPs by an organosilicon layer. The plasma deposition was performed in an axially-asymmetric capacitively-coupled RF ($f = 13.56 \text{ MHz}$) discharge that successfully combines sputtering of a metal target and plasma polymerization. Details about the plasma process are given elsewhere [16]. The discharge powered electrode (smaller electrode) was Ag-made target to bear the sputtering. For the sputtering step the plasma was maintained in pure argon at low pressure ($p = 5.4 \text{ Pa}$) with RF power of $P = 20, 40$ and 80 W ($V_{\text{dc}} = -546, -750$ and -1000 V , respectively). The sputtering time was fixed to 5 s or to 12 s. [16, 17].

The very thin SiOC:H cover layer was deposited in the same reactor after decomposition in the plasma of HMDSO at total pressure of $p_{\text{tot}} = 6.6 \text{ Pa}$. The power injected in the Ar-HMDSO plasma for this second step was $P = 80 \text{ W}$ which induced a bias voltage of $V_{\text{dc}} = -900 \text{ V}$.

B. Structural and optical characterizations

At each step of the elaboration process the samples were structurally and optically characterized. The size and surface density of AgNPs were determined after processing of Scanning Electron Microscopy (SEM) images. Optical transmittance spectra were recorded using a Hewlett Packard HP8452A Diode Array Spectrophotometer in the

UV-vis-NIR range (190–820 nm) to obtain the position of the AgNPs Local Surface Plasmon Resonance (LSPR). A Semilab 2000 spectroscopic ellipsometer was used to determine the thickness of the SiOC:H cover layer.

C. Electroluminescence characterization

EL measurements [13–15] were achieved under secondary vacuum ($<10^{-6} \text{ mbar}$) in order to avoid electrical discharges in the ambient. They were performed under ac voltage with variable frequency and electric field, up to 180 kV/mm, using cooled detectors; being a photomultiplier in photon counting mode for EL-field intensity and phase patterns, and a CCD camera coupled to a dispersive system for spectra acquisition.

III. RESULTS AND DISCUSSION

A. AgNPs Localized Surface Plasmon Resonance - LSPR

The mean size of the obtained AgNPs is smaller than 10 nm for the lowest applied power of 20 W and of $15 \pm 10 \text{ nm}$ and $20 \pm 10 \text{ nm}$ for the 40 W and 80 W, respectively. The AgNPs are organized in the plane in a single layer. Depending on the time of sputtering the size and density of AgNPs are different and the single plan can be discrete for short sputtering times (5 s) or percolated for longer sputtering times (12 s) at fixed power and pressure. The resultant organosilicon cover layer is conformal to the AgNPs. It is with thickness of only 6.5 nm.

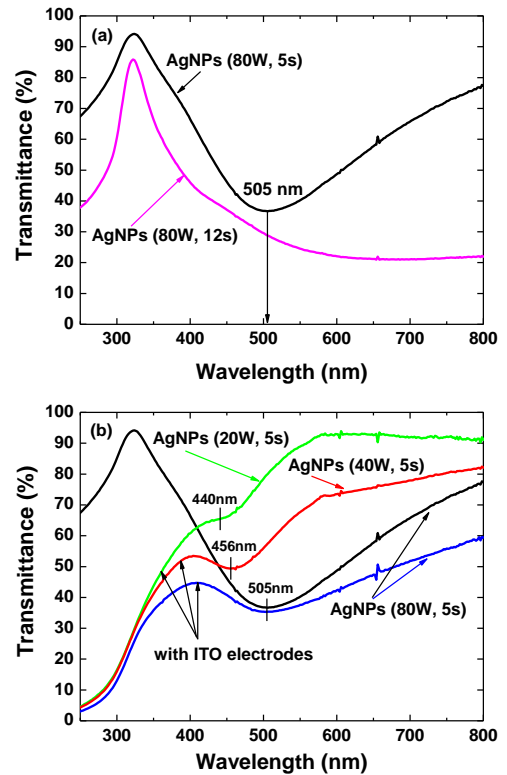


Figure 2. Transmittance spectra of the structures with AgNPs elaborated with different plasma powers and for different times: (a) Comparison between discrete ($P = 80 \text{ W}$, $t_s = 5 \text{ s}$) and percolated ($P = 80 \text{ W}$, $t_s = 12 \text{ s}$) AgNPs in terms of presence of LSPR of AgNPs and (b) Influence of the AgNPs size and ITO layers on the transmittance spectra.

UV-vis-NIR transmission spectra of the elaborated samples containing AgNPs are presented in Figure 2. The spectra for layers of discrete and percolated AgNPs are shown in Figure 2(a). One observes the LSPR of AgNPs (20 ± 10 nm size and surface density of 2×10^{11} NPs/cm²) of the discrete structure at 505 nm. The LSPR disappears when the AgNPs are percolated in the layer. When elaborated with lower plasma power the AgNPs are smaller in size and their LSPR is blue shifted as shown in Figure 2(b). However, the AgNPs size variation gives the possibility to probe different chemical bonds in the BOPP structure. The influence of the conductive ITO electrodes is also shown in Figure 2(b). One can notice that the conductive ITO electrodes limit the analyses to the visible range, which is in accordance with the targeted energies.

B. Enhancement of the electroluminescence intensity

EL-intensities of bare BOPP sample and of the AgNPs/SiOC:H tailored one as function of the applied electric field are shown in Figure 3. One can clearly notice the very strong enhancement of the EL-signal in presence of AgNPs. Actually, the plasmon induced enhancement of the EL spectrum can be more than 3 orders of magnitude. Moreover, the detection threshold is much lower. Even with a field of 10 kV/mm the BOPP signature becomes readable. It was previously shown that switching from gold to ITO electrodes produced a decrease in the EL emission from BOPP along with a change in the shape of the EL-field characteristic in which the bump-like shape obtained for Au-electrodes disappears with ITO. This was explained by the contribution from surface plasmon (SP) emission in the red domain [10, 14, 15] in case of gold; such emission being dominating at low ac field.

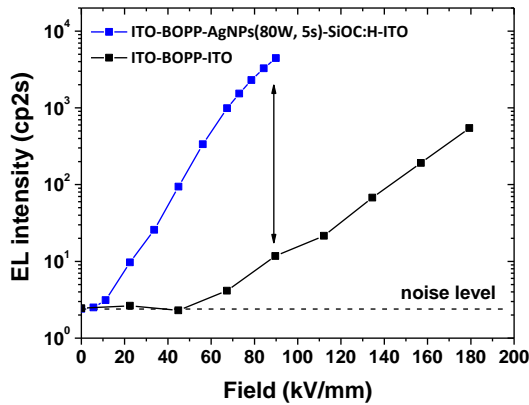


Figure 3. Electroluminescence vs. electric field under 50 Hz ac stress of bare and tailored BOPP films.

There are indeed different possibilities for the enhancement of the EL intensity: (i) stronger excitation, meaning larger number of recombination events; (ii) larger quantum yield (larger probability for radiative recombination); (iii) AgNPs contribution to the emission signal. To get further into the underlying process, complementary information is achieved through phase-resolved EL patterns and EL emission spectra.

Figure 4 compares the EL phase patterns obtained without and with the AgNPs/SiOC:H nanocomposite stack. Data are obtained at different applied electric fields owing to the strong difference in the EL yield (Figure 3). One can clearly see that there is no strong dependence of the shape of the pattern on the electric field and that the advance of phase is not largely pronounced in presence of AgNPs. This appears to be a quite distinct behavior compared to results obtained with Au electrodes where in general the advance of phase is larger when the SP emission is dominant [15].

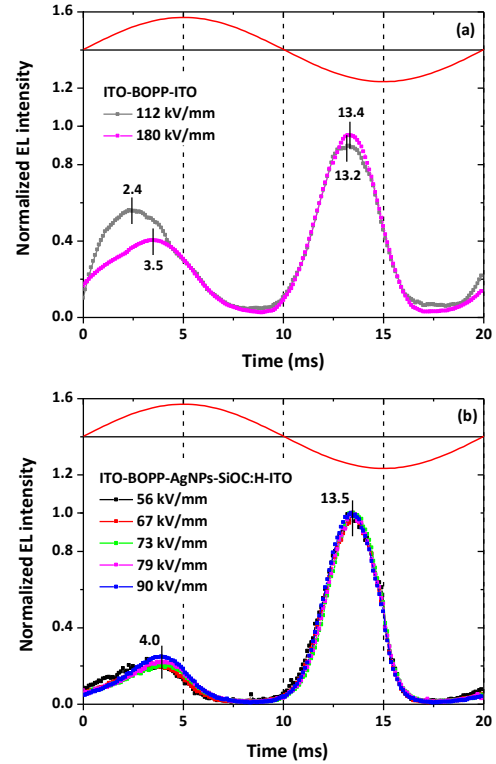


Figure 4. Phase-resolved EL patterns obtained on (a) BOPP and (b) one side tailored BOPP by an AgNPs/SiOC:H nanocomposite stack.

We have shown previously that the EL spectrum of BOPP, and more generally of polyolefins, can be deconvoluted into different contributions peaking at 415, 505 and 570 nm, all of these bands being characteristic of existing defects or created chemical functions into the material [10, 14, 15]. Combined with the absorbance spectrum of the AgNPs/SiOC:H tailored BOPP film (Figure 5) one can realize the strong coupling at the same energy (2.45 eV or $\lambda = 505$ nm) between the LSPR of the AgNPs and the contribution of recombination-induced luminescence involving conjugated CC bonds bound to CO species [14]. Moreover, the spectrum obtained for tailored with AgNPs BOPP films (Figure 5) reveals the presence of an additional band at about 650 nm that does not appear in the spectra obtained on bare BOPP (not shown here). In case of Au-electrodes an extra broad emission at 700-750 nm was attributed to the SP emission [14]. The additional band at 650 nm can be attributed to the SP emission from the AgNPs in SiOC:H environment.

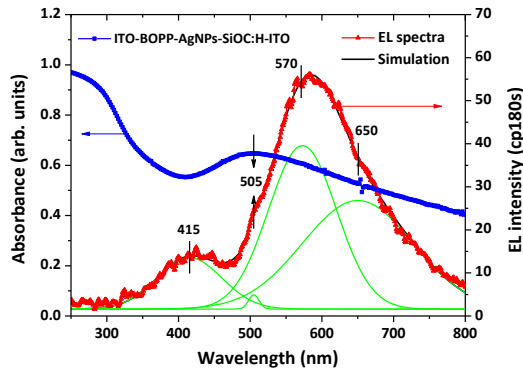


Figure 5. Absorbance and ac-EL spectrum of an one side tailored BOPP by an AgNPs/SiOC:H nanocomposite stack. The EL spectrum is obtained with an ac crest field of 90 kV/mm. The spectrum is deconvoluted into the sum of different Gaussian functions with peak wavelength indicated in the figure.

However, this does not constitute the only explanation to light enhancement. Other possibilities are to be considered. Firstly, the AgNPs/SiOC:H layer may favor charge injection, and then charge trapping on the AgNPs. The number of recombination events might be amplified by combining the enhanced charge injection efficiency and the capability of AgNPs to stabilize injected charges [16]. Second, a sensitization of the PP due to the presence of AgNPs may occur, either through the formation of oxidized groups in the AgNPs environment, or through metal enhanced luminescence processes, that involve the LSPR in presence of metallic nanoparticles. This later process, complex indeed, has been recently reported in different nanoscience fields [18, 19].

IV. CONCLUSION

Evidences on the possibility to change energetics of the charge carriers near the interface is brought by electroluminescence measurements on tailored by AgNPs interfaces of capacitor films. Not only the light intensity is found much stronger in presence of AgNPs, but the detection of light emission starts at lower field. Such strong emission is most likely due to a radiative surface plasmon relaxation from the AgNPs in organosilicon environment. Depending on the size and density of AgNPs one can obtain different levels of energy absorption at the LSPR, thus providing flexibility for further enhancement of the response, according to probed material. Further work will be directed to explore the metal enhanced electroluminescence process by considering the localized surface plasmon resonance in presence of AgNPs in order to probe structural modifications and subsequent aging of polymeric insulations.

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